

UDC 666.1.056

PROPERTIES OF A GLASS SURFACE MODIFIED BY A NEW FROSTING PASTE. SURFACE MORPHOLOGY

O. N. Sidel'nikova¹ and A. N. Salanov¹

Translated from *Steklo i Keramika*, No. 12, pp. 10 – 13, December, 2007.

A new paste is proposed for frosting glass surfaces. The action of the paste is based on the physical-chemical process of surface chemical ion exchange. The paste does not contain hydrofluoric acid or its derivatives. The frosting process occurs at 300°C and differs substantially from the existing frosting processes — chemical etching and sandblasting. The morphology of the surface layer of the frosted glass is characterized by a system of microblocks (linear dimensions 50 – 150 μm) and microcracks (width 100 – 200 nm). The microblocks have even faces and a smooth frontal surface. The surface morphology of the glass is the same after frosting and subsequent deposition of a metal by chemical reduction.

It is well-known that an important factor in the deposition of organic or inorganic coatings on a glass surface is the adhesion power of the glass, which acts as a substrate. Modification of the structure of the surface layer of glass by, specifically, frosting can change the surface roughness substantially and, in consequence, increase the adhesion power of the glass as a substrate per unit area of the geometric surface.

Sandblasting with solid abrasive particles and chemical etching of a glass surface by solutions containing hydrofluoric acid or its derivatives are now widely used for frosting glass.

A new method of frosting glass is applying a paste (RF Patent No. 2238919) [1, 2], which does not contain hydrofluoric acid or its derivatives and acts on the basis of surface ion exchange processes [3, 4]. The present article gives the results of a comparative investigation, by the method of electron scanning microscopy, of the morphological structural properties of the surface layer of glass modified by sandblasting, chemical etching, and treatment with the new frosting paste (NFP) which contains no hydrofluoric acid. The structure of the surface layer of glass after frosting by chemical etching and by using the NFP followed by deposition of a thin layer of silver by chemical reduction was also investigated.

Samples of sodium-calcium-silicate glass (GOST 111–2001) were used. Chemical etching was performed by fluorine-containing paste for frosting glass, prepared following the recommendations presented in USSR Inventor's Certificate No. 948926A. The duration of the chemical etching of the glass samples was 5 – 10 min.

The glass surface modification process NFP consisted of the following stages [1, 2]:

- degreasing the surface and washing with warm flowing water;

- depositing a layer of paste on the glass surface with an appropriate tool using a stencil consisting of a film manufactured by the ORACAL Company and prepared by plotter cutting, or using a silkscreen form;

- removing the stencil, if it was used at the preceding stage;

- heat-treatment of the glass sample at approximately 300°C for 15 – 20 min;

- removing the dry layer of paste by washing in warm flowing water.

A doctor was used to deposit the paste layer on the surface of the glass. The thickness of the paste layer deposited on the glass when using a stencil consisting of an ORACAL film was approximately 50 μm, but it was impossible to obtain in this case a uniform deposition of paste on a glass surface with a substantial area (> 100 cm²). When using a silkscreen form the paste is deposited uniformly on the glass, but the area of the glass with a uniform layer of paste is determined by the working surface area of the silkscreen form.

Electron microscope investigations of the glass surface were performed with a JSM-6460RV scanning electron microscope (Jeol, Japan). First, a thin layer of platinum (100 Å thick) was deposited (JFC-1600) on glass samples without a metal coating in order to make the surface layer of the glass conducting. Glass samples which were not subjected to the treatment methods indicated above were used as samples with a smooth surface (Fig. 1).

¹ Institute of the Chemistry of Solids, Moscow, Russia; G. K. Boriskov Institute of Catalysis, Moscow, Russia.

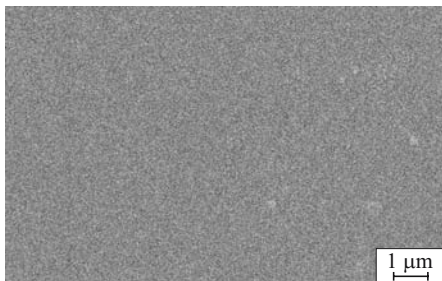


Fig. 1. Electron microscope photograph of a smooth glass surface ($\times 10,000$).

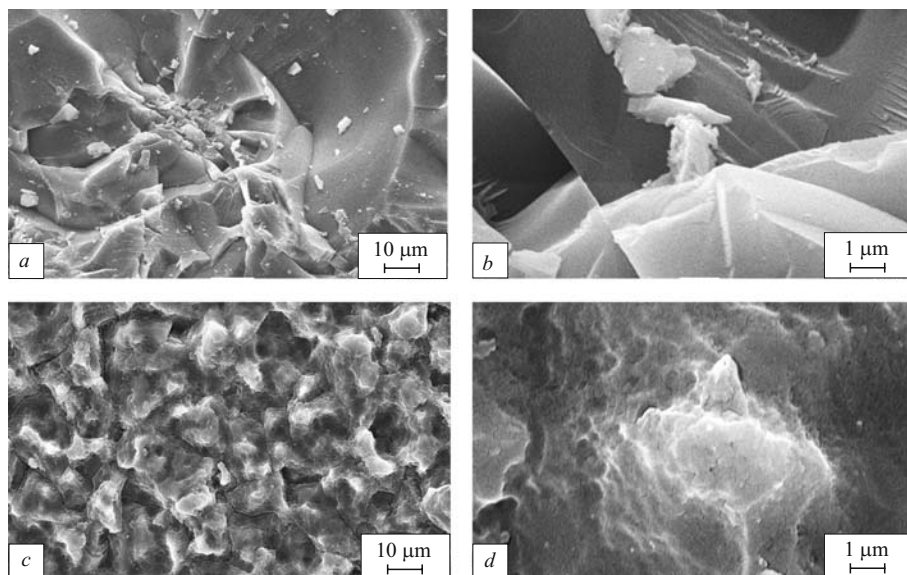


Fig. 2. Electron-microscope photographs of a glass surface ($\times 1000$ and $10,000$): *a* and *b*) after sandblasting; *c* and *d*) after chemical etching.

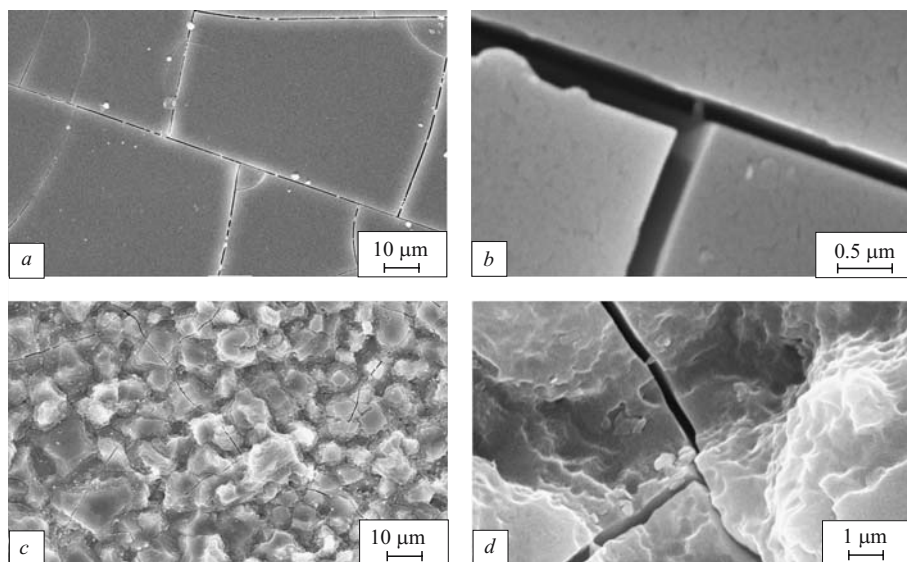


Fig. 3. Electron-microscope photographs of a glass surface ($\times 1000$ and $10,000$): *a* and *b*) after treatment with the new frosting paste; *c* and *d*) after treatment with the new frosting paste together with preliminary chemical etching.

Sandblasting produces a rough, mechanically stressed, surface structure (Fig. 2*a* and *b*).

Chemical etching of a glass surface using compositions containing hydrofluoric acid or its derivatives is well-known and has been widely used since the second half of the 19th century. Chemical etching produces a glass surface with microrelief, less mechanically stressed than the surface glass obtained after sandblasting (Fig. 2*c* and *d*).

The nonuniform etching of glass on different sections of the surface could be due to the presence of adsorbed particles on the glass surface, microdefects of the structure, and non-uniformities of the glass composition and surface layer. The main drawback of chemical etching for treating glass, which substantially limits its use in commercial decoration of glass, is the presence of chemical reagents (hydrofluoric acid or its derivatives), which are dangerous for health, and the solutions and pastes used for chemical etching.

Treating glass with the new frosting paste (RF Patent No. 2238919), which does not contain hydrofluoric acid or its derivatives, differs from the glass decoration methods indicated above [1, 2]. The frosting process is accompanied by surface ion exchange of Na^+ in the glass on Li^+ ions diffusing from the paste to the surface of the glass. This ion exchange process is characterized by a decrease of the volume of the product as compared with the volume of the initial glass. The shrinkage factor (ratio of the volume change in the course of the reaction to the initial volume of the glass) is 5% [4]. Such large shrinkage results in the accumulation of mechanical stresses in the surface layer of the glass and, in consequence, the appearance and propagation of microcracks.

A microblock structure with a network of cracks arising in the surface layer of glass as result of treatment of the glass with NFP can be seen in the electron microscope photographs (Fig. 3*a* and *b*). The size of the blocks is approximately 20 – 150 μm , and the width of the microcracks is 100 – 200 nm. The frontal surface of the microblocks remains smooth, like the initial untreated surface of the glass (see Fig. 1). The thickness of the modified surface layer of the glass with a microblock structure and the network of cracks depend on the thickness and

composition of the NFP layer deposited as well as on the conditions under which the frosting process is conducted. The modified surface layer of the glass is approximately 50 μm thick.

Comparing the electron microscope photographs (see Figs. 2*a, b* and 3*a, b*) shows that the structure of the surface layer of the glass characteristic for NFP treatment differs substantially from the corresponding structure obtained by sandblasting and chemical etching. This difference apparently determines the difference in the color hues of surface sections in the case where NFP is used. Thus, after treatment by the NFP method of surface ion exchange, the surface layer of the glass has a milky white color with weak scattering of light, while the glass after sandblasting and chemical etching has a semi-transparent hue with strong light scattering.

If the glass samples are first chemically etched and then frosted using the NFP, then the resulting surface relief has features which are characteristic for the first and second processes (Fig. 3*c* and *d*). It should be noted that in this case the boundaries of the microblocks are not as even as in case of only frosting with NFP. Apparently, the microrelief formed at the first stage of chemical etching of glass promotes the development of additional locations where relaxation of the microstresses that arise with the appearance and propagation of microcracks during the second stage — the surface ion exchange process — occurs.

If the glass treatment sequence is reversed, i.e., first frosting with NFP followed by chemical etching, then the structure of the surface layer of glass will change substantially (Fig. 4). The microcrack network formed at the first stage (NFP etching) is a source of locations on the glass surface for preferential dissolution. As a result, the surface structure formed is much rougher than the structure arising with only chemical etching or only frosting using NFP (see Figs. 2*c, d* and 3*a, b*) as well as the structure rising with chemical etching followed by frosting with NFP (see Fig. 3*c* and *d*). Such a change in the surface morphology can change the surface properties of the glass substantially, which depend on the roughness of the surface, for example, the specific area of the glass surface, the adhesion strength of coatings on glass, and so forth.

The morphological features which arise on a glass surface after frosting with NFP (with or without chemical etch-

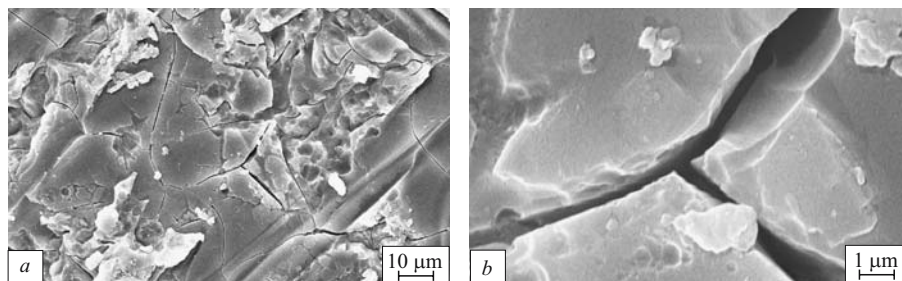


Fig. 4. Electron-microscope photographs of a glass surface ($\times 1000$ and $10,000$): *a* and *b*) after treatment with NFP followed by chemical etching.

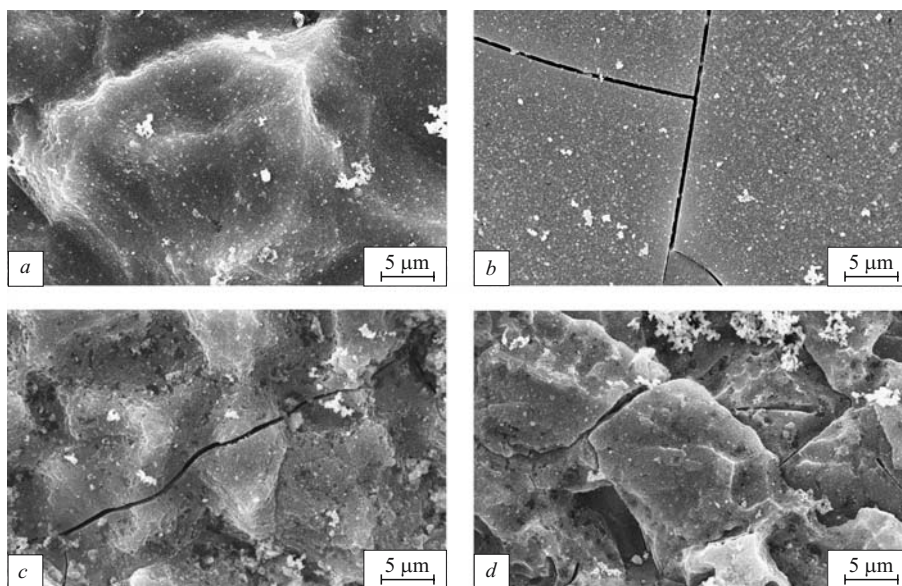


Fig. 5. Electron microscope photographs of the glass surface with a 230 nm thick, chemically deposited, layer of silver ($\times 3000$): *a*) after chemical etching; *b*) after treatment with NFP; *c*) after treatment with NFP and pretreatment by chemical etching; *d*) after treatment with NFP followed by chemical etching.

ing) could be of great value for subsequent deposition of organic or inorganic compounds by chemical, electrochemical, physical, or other methods.

We investigated the morphology of a surface layer of glass with a metal coating, specifically, with a layer of silver deposited on the glass by chemical reduction.

The chemical reduction of Ag^+ ions to metallic Ag was conducted in chemical silvering solutions based on ammonia complexes of silver in the presence of glucose as a reducing agent. The chemically deposited layer of silver was approximately 230 nm thick. The thickness was measured by chemical and electrochemical analysis by determining the Ag^+ concentration in solution after the layer of silver chemically deposited on the glass surface in a dilute (1 : 3) nitric acid solution was dissolved. The thickness of the silver layer deposited by chemical reduction can be decreased by decreasing the duration of the deposition process; specifically, silver layers up to 20 nm thick were deposited.

Figure 5 displays photographs of an approximately 230 nm thick surface layer of silver, chemically deposited on a glass surface after frosting with NFP with and without chemical etching. The size of the globules in the silver layer reaches 100 nm, and the morphology of the surface reflects the surface morphology after the corresponding frosting of the glass, which can be seen by comparing Figs. 5a and 2c, d (glass treated by chemical etching), Figs. 5b and 3c, d (glass treated with NFP with preliminary chemical etching), Figs. 5c and 2a, b (after treatment with NFP), and Figs. 5d and 4a, b (after treatment with NFP followed by chemical etching). The more extended glass surface with a chemically deposited layer of silver is formed in the latter case, specifically, after treatment of glass with NFP followed by chemical etching (see Fig. 5d).

In summary, it can be concluded that the morphology of the surface layer of glass in the case where the new paste is used for frosting, acting on the basis of surface ion exchange (including combined with preliminary or subsequent chemical etching), differs substantially from the surface morphology characteristic for sandblasted or chemically etched glass. Changing the conditions of frosting using NFP, resulting in the formation of a characteristic surface layer structure of the glass, can have a strong effect on important properties,

such as the adhesion strength of coatings (organic or inorganic) deposited on the glass as well as other physical-chemical properties of the surface layer of glass.

We thank A. N. Serkova, Candidate of Chemical Sciences T. P. Aleksandrova, N. M. Zakharova, Candidate of Chemical Sciences A. A. Sidel'nikov, and Corresponding Member of the Russian Academy of Sciences N. Z. Lyakhov for assistance and interest in this work.

REFERENCES

1. O. N. Sidel'nikov, A. A. Sidel'nikov, and D. V. Svistunov, "The new glass frosting paste," *Glass*, No. 3, 12 (2006).
2. O. N. Sidel'nikova, A. A. Sidel'nikov, and D. V. Svistunov, "New paste for frosting glass," *Steklo Keram.*, No. 4, 30–31 (2006).
3. S. A. Chizhik and A. A. Sidel'nikov, "Kinetics of solid-phase reactions with positive feedback between the reaction and fracture. 1: Quantitative model of the motion of a fracture front," *Izv. Akad. Nauk, Ser. Khim.*, **4**, 626–631 (1996).
4. S. A. Chizhik and A. A. Sidel'nikov, "Kinetics of solid-phase reactions with positive feedback between the reaction and fracture. 2: Kinetics of ion exchange in alkali-silicate glass," *Izv. Akad. Nauk Ser. Khim.*, **4**, 632–636 (1996).